Book Reviews

Complex Compounds of Transuranium Elements. By A. D. GELMAN, A. I. MOSKVIN, L. M. ZAITSEV, and M. P. MEFOD'EVA. Translated from Russian by C. N. Turton and T. I. Turton, Consultants Bureau, New York, N. Y., 1962. 195 pp. 16 × 23.5 cm. Price, $12.50.

As the result of a relatively large scale production program in the U. S. Atomic Energy Commission, the transuranium elements from $Z = 93$ to $Z = 99$ should be much more easily available to inorganic chemists in the next few years. Since Russian chemists have been active in research on the aqueous chemistry of these elements, this book is a timely report on the present knowledge in the area. The authors have done a satisfactory, though not complete job of referring to western work. However, the major value of the book lies in the inclusion of data tables, graphs, spectra, etc., from Soviet research which are less readily available to chemists in the United States. Separate chapters discuss the complexation in aqueous solutions of neptunium, plutonium, and the transplutonium elements in their various oxidation states by inorganic and organic ligands. Short sections at the end of the chapters on neptunium and plutonium deal with the isolation of complex compounds of these elements; however, throughout the book the emphasis is placed on the complex species present in aqueous solutions. A final chapter rather briefly reviews the application of complexes in the separation of the transuranium elements.

The quality of Russian work in this area of chemistry is good and, in general, has had a more basic orientation than much of the western research. The major defect in this book is the almost total absence of critical evaluation. The data are reported without discussion either as to the value or the fundamental implications. A second but not unrelated defect is the lack of any discussion on similar research with corresponding lanthanide elements. The lanthanide–actinide analogy is such a dominant feature of the chemistry of the trivalent ions that the chemist studying actinide complexes must be mindful of its implications. Despite these omissions, this book is recommended, since it makes apparent the vast amount of research which is still to be done on these elements. The quality of the translation is exceptionally good and the errors both in printing and in statement by the authors are few and minor.

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Chrom, Teil A Lieferung 1, System-Nummer 52, 8 Auflage, Gmelins Handbuch der Anorganischen Chemie. [Chromium, Part A Section 1, System Number 52, 8th Edition, Gmelins Handbook of Inorganic Chemistry.] Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse, 1962. xx + 418 pp. 17 × 24.5 cm. In German. Price, $79.00.

The appearance of each new portion of the Gmelin Handbuch is welcomed by many persons. Previous complimentary remarks will apply equally to this first part of the chromium volume, which is devoted mainly to the geology of chromium, the technology of the element and its compounds, and the physical properties of the metal, plus a brief historical survey and an excellent ten pages on physiological effects. As in earlier volumes, the organization is extremely systematic and lucid, and the Table of Contents gratifying thorough; in addition, English marginal titles have been inserted.

According to the publisher, the literature has been completely reviewed through 1949, but beyond that, only in some instances. To point out that certain portions (notably Physiology and most of Geology) are much more up-to-date than others is more a tribute to a few of the compilers than a criticism of the rest. However, parts of the 95-page Technology section seem to contain very few references from even the 1940's. Additionally (and recognizing that the separate portions of a group effort will reflect varying degrees of completeness at cut-off time, and that much new information must be omitted) it is to be regretted that old attitudes as well as old ideas survive in a few places. Thus, for example, the 1924 report that the role of sulfuric acid in the electrolytic reduction of chromic acid (p. 218[1]) is to cause formation of $Cr_2(SO_4)_3$ could at least have been modified in the light of elementary coordination chemistry, if not wholly replaced by the more specific interpretations of Knorr and others.

In any case, the pointing out of minor faults in so large a work ought to be accompanied by liberal praise for the value of the product: certainly the stated aim of the Gmelin Institute, "to evaluate in retrospect the entire subject matter from the point of view of modern knowledge, and to extract from the obsolete material the kernel which can be of value to us today," continues to be met in each succeeding volume.

(1) This is not the least modern section.

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Infrared Spectra of Inorganic and Coordination Compounds. By K. NAKAMOTO. John Wiley and Sons, Inc., 605 Third Avenue, New York 16, N. Y., 1963. xii + 302 pp. 14.5 × 23 cm. Price, $9.50.

Although newer spectroscopic tools have captured the limelight in recent years, infrared spectroscopy continues to provide much useful information to the chemist. The literature of infrared spectroscopy therefore continues to grow at a rapid pace. Nakamoto's book provides a comprehensive guide to this literature for a fairly well defined area of chemical interest.

The book is in four parts. Part I, "Theory of Normal Vibrations," is too highly condensed to be very useful. The tenor of much of the material in these 65 pages is somewhat out of keeping with that of the book as a whole. There is a real need (which Professor Nakamoto is admirably qualified to answer) for a thorough and candid discussion of the capabilities and limitations of normal coordinate analysis. It is all very well to explain the principles invoking in carrying out a normal coordinate analysis, but what do the results mean? How realistic are the potential energy functions employed? How sensitive are the calculated frequencies to the choice of force constants? What is the basis for comparison of observed and calculated spectra? Should one employ observed or harmonic oscillator-adjusted frequencies in such comparisons? What are the effects of Fermi resonance? These and many other questions are relevant to an intelligent interpretation of the results of normal coordinate analysis, but they are not discussed from a critical point of view in this book. The great majority of chemists who make use of the infrared literature will never carry out a normal coordinate analysis, but they should be able in some measure to critically evaluate the results of such studies.

The considerable value of Nakamoto's book rests largely on Parts II and III, in which the infrared literature of inorganic and coordination compounds is thoroughly reviewed. Nearly a thousand references are given for these two parts.

On the whole the reporting is concise and accurate. A few erroneous statements occur here and there. For example, the statement regarding cyclopropane on p. 229 is precisely what the

reference cited disproves. There is also a certain lack of critical judgment in some places where it appears called for. As an example, in discussing dinitrogen difluoride (p. 102), the statement is made that it exists as *trans*-1,2-difluorodiazine and 1,1-difluorodiazine. It is further stated that (reference cited). . . "has confirmed these structure by infrared spectra." Granted that N_2F_2 is a simple compound; the use of the word "confirmed" nevertheless reveals, in the reviewer's opinion, an overly sanguine view of what can generally be accomplished with infrared methods. It is worth noting that recent microwave spectral and electron diffraction studies strongly indicate that the second N_2F_2 isomer is *cis*-1,2-difluorodiazine.

Part IV of the book consists of appendices: character tables, *F* and *G* matrix elements for simple molecular types, an outline of a normal coordinate analysis of metal acetylacetonates, a wave length to wave number conversion table, and group frequency correlation charts.

Despite whatever critical comments I have felt compelled to make, I do feel that Nakamoto has written an excellent book which deserves wide use. An abundance of tables and diagrams adds greatly to the book's utility as a reference source. Any chemist who makes use of infrared spectroscopy will find this volume a valuable addition to his bookshelf.

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Inorganic Syntheses. Volume VII. Edited by JACOB KLEINBERG. Inorganic Syntheses Series, McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y., 1963. xi + 253 pp. 15 × 23.5 cm. Price, $8.95.

"Inorganic Syntheses," Volume VII, contains 65 independently tested and checked preparations. Only ten of these represent alternative procedures for preparing compounds previously listed in earlier volumes of the series. The editor appears to have maintained the high standards set by his predecessors. Format and general organization employed in previous volumes have been retained. Chapter headings are the Mendeleev periodic subgroups. The placement of compounds in chapters is determined by the principal element in the compound. Author, formula, and subject indexes are cumulative. A total of 454 syntheses are listed for the entire series.

While the transition metals are represented predominantly by classical complexes in Volume VII, preparations are also given for some cyclopentadienyl carbonyls and their derivatives, triiron dodecacarbonyl, and sodium salts of carbonyl hydrides. Of the representative elements noteworthy preparations of compounds of gallium, indium, silicon, germanium, phosphorus, and sulfur are listed. Syntheses of isotopically labeled Na_2S^{35}, S^{35}, NaF^{18}, H^2Cl^{36}, $SOCl_2^{36}$, $SiCl_4^{36}$, BCl_3^{36}, $GeCl_4^{36}$, PCl_3^{36}, $Fe^{55,59}(C_2H_5)_2$, and $Fe^{55,59}(C_2H_5)_2^+$ are given also.

Volume VII represents a useful addition to the "Inorganic Syntheses" series.

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Solubility Constants of Metal Oxides, Metal Hydroxides and Metal Hydroxide Salts in Aqueous Solution. Edited by W. FEITKNECHT and P. SCHINDLER. International Union of Pure and Applied Chemistry. Butterworths, London, England, 1963. v + 69 pp. 15.5 × 24.5 cm. Price, $2.25.

Several years ago a project was undertaken by a Subcommission of the Analytical Section of I.U.P.A.C. to compile literature data on solubility products of inorganic substances and stability constants of metal ion complexes.

The present monograph is an extension of this work. The critical survey of solubility data in aqueous solution of metal oxides, metal hydroxides, and metal hydroxide salts includes the following members of the periodic table: Be, Mg, Ca; Sc, Y, and the rare earths; Ti, Zr, Hf, Th; Cr, Mn, Fe, Co, Ni; Cu, Ag, Au; Zn, Cd, Hg; Al, Ga, In, Tl; Sn and Pb. In several cases where the substance exists in more than one form, solubility data are given for each form. In some cases, also, data are given for more than one oxidation state of the metal. The monograph should be quite useful not only as a reference for solubility data, but also in setting a pattern for reporting such data.

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Nonstoichiometric Compounds. Advances in Chemistry Series, No. 39. ROLAND WARD, Symposium Chairman. American Chemical Society, 1155 Sixteenth Street, N.W., Washington 6, D. C., 1963. vii + 253 pp. 15.5 × 23.5 cm. Price, $7.00.

This volume is a collection of papers presented at the symposium on nonstoichiometric compounds sponsored by the Division of Inorganic Chemistry at the American Chemical Society meeting in March, 1962, at Washington, D. C. All of the papers, including review papers by A. D. Wadsley, G. G. Libowitz, J. S. Prener, and M. J. Sienko, were invited. In addition, J. S. Anderson contributed a more general survey on "Current Problems in Nonstoichiometry" as the introductory paper. Twenty-three papers, ranging in length from six to fourteen pages, comprise the volume.

A wide range of phenomena and structural concepts can be included under the heading of nonstoichiometric compounds, and a good sampling of this variety is found in this symposium. Anderson's opening paper deals with the problems associated with a thermodynamic treatment of defect structures. Wadsley's paper on the metallic oxides points out relationships between the crystal structures of some nonstoichiometric phases and the structures of chemically similar substances of fixed composition in which the different phases are ordered and identifiable. In a paper on the metal hydrides, Libowitz describes an attempt to interrelate the interaction energy of hydrogen vacancies, the hydrogen content, and the equilibrium pressure of hydrogen above a hydride. Prener takes up the chalcogenides and outlines a statistical thermodynamic theory for predicting the equilibrium concentration of lattice defects. His paper includes a review of crystal structure data on the chalcogenides. Sienko's paper is primarily devoted to the transport and magnetic properties of the tungsten and vanadium bronzes, and these properties are discussed in terms of a band model. Each of these review papers provides an excellent summary of the current situation in the particular area of nonstoichiometric compounds. Shorter but equally authoritative reviews are contributed by L. Kihlborg on molybdenum oxides, by L. E. J. Roberts on fluorite-type oxides, and T. R. P. Gibb on metal hydride models. The remaining fifteen papers, of a total of 23, report new research results.

The value of such a collection of symposium papers may be questioned on several counts, none of which relates to the nature or quality of the papers themselves. First of all, for whom are such publications intended? This volume, and several others in the Advances in Chemistry series, strike me as being too advanced and parochial to serve as a good introduction or survey for one just entering the field or for the casual seeker of information. On the other hand, a person active in this particular area of inorganic chemistry finds that the time lapse between the symposium and the publication of the papers, over a year in this case, makes the volume of relatively minor use. Happily, some of the authors have compensated somewhat for the delay by including later information and by making revisions on the basis of the discussions at the symposium.